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THE SEPARATION AND CONTROL OF TRITIUM STATE-OF-THE-ART STUDY

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THE SEPARATION AND CONTROL OF TRITIUM

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By

L. L. BURGER

April 14, 1972

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16. Abstracts

The properties of tritium are briefly reviewed, and the potential problem resulting from tritium production in power reactors is surveyed. It is seen that in about two decades the rate of production and the increasing world inventory may dictate controlled storage of tritiated waters. The known methods for deuterium separation(heavy water production) have been surveyed and then considered for tritium separation.

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THE SEPARATION AND CONTROL OF TRITIUM

STATE-OF-THE-ART STUDY

I. INTRODUCTION

The control of tritium is of increasing concern to the power reactor industry. Leakage of fission tritium, production from chemical shims, from control rods, from n-capture by water, from impurities in construction materials--can bring the concentration up to the μCi/ml level in reactor coolant and the release to the environment is a potentially serious adverse consequence of the extensive use of nuclear fission and fusion power sources. The present trend appears to be toward zero release to the environment. However, this approach substitutes an in-plant problem and only postpones the environmental one and either an acceptable means must be found for releasing tritiated water or a method for separation (concentration) and permanent storage must be developed. The problem, of course, is also an important one for the fuel reprocessing plants which handle 50-90% of the tritium produced in the reactors.

The projected growth of thermal power reactors indicates that in about two decades a production equal to the world's natural tritium inventory will be reached. In addition, the development of fusion power will add greatly to the tritium inventory. Thus, it is important to consider the development of simple, economic methods to lower the tritium concentration of process water to specified levels as well as to concentrate and store highly enriched tritiated water.

II. PROPERTIES OF TRITIUM

Tritium, the hydrogen isotope of mass three, decays by β-emission to ^{3}He with a half life of 12.26 years. There is no gamma radiation and the low energy of the β (0.0186 MeV max, 0.0057 MeV average) suggests that there would be little radiation damage from the decay. The rapid diffusion of hydrogen isotopes means that tritium is difficult to contain. Once in the environment, it enters biological materials rapidly. In the atmosphere it equilibrates with water at a rate of 0.2 to 3% per day and is most commonly encountered in the form of water vapor.[1] Thus, although tritium is usually classed as one of the least hazardous radioisotopes, its rapid assimilation by biological systems makes it of special concern to personnel who work with high concentrations. Also, the half life of 12.3 years means that any increased production rate must be carefully evaluated in terms of long range effects.

Unlike the isotopes of other elements, the relatively large mass differences of H, D and T cause appreciable differences in properties of the elements and their compounds. Table I lists some physical properties of the isotopic forms of hydrogen. The data used are largely from Mittelhauser and Thodos.[2] Jacobs[3] has reviewed other data and sources.

Tritium gas in the atmosphere combines with oxygen to form water vapor. The equilibration with water has been noted. Because of the low concentration relative to H, the predominant form will be HTO. Some properties of tritiated water are compared with other water species in Table II.

The chemical properties of tritium differ slightly from those of the lighter isotopes for two reasons: 1) the greater mass of

TABLE I

PHYSICAL PROPERTIES OF ISOTOPIC HYDROGEN SPECIES

	H_2 [a]	HD	HT	D_2	DT	T_2
Mol wt	2.016	3.022	4.025	4.029	5.032	6.034
Boiling pt, °K	20.39	22.14	22.92	23.67	24.38	25.04
Triple pt, °K	13.96	16.60	(17.62)	18.73	(19.71)	20.62
Triple pt press, mm	54.0	92.8	(109.5)	128.6	(145.7)	162.0
Critical temp, °K	33.24	35.91	(37.13)	38.35	(39.42)	(40.44)
Critical press, mm	9736	11134	(11780)	12487	(13300)	(13878)
Dissoc. En, eV [4]	4.476	(4.511)	(4.524)	4.553		4.588
Zero pt En., cm^{-1} [5,6]	2171.4	1884.3		1542.4		

(a) The normal state (high temperature ortho-para composition) is used for this table. The "equilibrium" state, the composition existing at the normal boiling point gives slightly different properties.

TABLE II

PROPERTIES OF OXIDES OF H ISOTOPES [6,7]

	H_2O	HDO	D_2O	T_2O	HTO
Mol wt	18.015	19.021	20.028	22.033	20.024
bp °C	100.00		101.42	101.51	
Triple pt	0.010		3.82	4.49	
ΔH_v (100°C), kcal	9.72	9.8	9.93	10.1	9.9
Max dens/temp	0.999973/3.98		1.1059/11.2	1.2150/13.4	
Density, g/ml, 25°C	0.9967		1.1044	1.2138	
Vapor Pressure, mm, 25°C	23.8	22.12	20.6	19.8	21.7

tritium and lower zero point energy of tritium compounds, and 2) the radiation induced reactions. The former, in addition to significantly changing the physical properties as shown in Tables II and III, also shift the equilibrium for various reactions. Libby[8], Bigeleisen[9,10] and others have made theoretical and experimental analyses of these effects. In general, the heavier isotope will concentrate in molecules having higher vibrational energy. Thus one finds for the exchanges:

$$HT + H_2O \rightleftharpoons HTO + H_2, \quad K = 6.0$$

$$HD + H_2O \rightleftharpoons HDO + H_2, \quad K = 3.5$$

The second effect, radiolysis reactions induced by the β emission, results in the incorporation of the tritium atom into many otherwise relatively unreactive molecules. Kandel[11] measured the reaction rate of tritium with methane and found that the initial product, CH_3T, reached a maximum concentration in about 12 hours. Many other reactions have been studied in considerable detail such as the simple H_2-T_2 exchange[12], the oxidation in air[13,14] and biological exchange reactions[15,16].

The environmental and physiological aspects of tritium and the detection and determination of tritium will not be covered in this report.

III. SOURCES AND PRODUCTION OF TRITIUM

Tritium is produced by many nuclear reactions. Some of the more important ones are listed in Table III.

TABLE III

COMMON SOURCE REACTIONS FOR TRITIUM

1) $^{2}H + {}^{2}H \rightarrow {}^{3}H + n$

2) $^{9}Be + {}^{2}H \rightarrow {}^{3}H + {}^{8}Be$

3) $^{2}H + n \rightarrow {}^{3}H$

4) $^{14}N + n \rightarrow {}^{3}H + {}^{12}C$

5) $^{16}O + n \rightarrow {}^{3}H + {}^{14}C$

6) $^{6}Li + n \rightarrow {}^{3}H + {}^{4}He$

7) $^{10}B + n \rightarrow {}^{3}H + {}^{8}Be$

8) $^{11}B + n \rightarrow {}^{3}H + {}^{9}Be$

9) U, Pu, Th fission

10) photonuclear, $(\gamma, {}^{3}H)$

Reactions 4) and 5) are largely responsible for the natural production of tritium in the atmosphere. Reactions 1) and 2) are typical bombardment type reactions--of interest in high energy physics but not of great concern to the present discussion. The remaining reactions represent to some degree contributions from nuclear power reactors.

The cosmic ray induced reactions in the atmosphere produce tritium at a rate estimated as high as 2 tritons/cm^2-sec*. Nir[17] after reviewing the previous data calculates a rate of about 0.19/cm^2-sec corresponding to a steady state value of about 2.6×10^7 Ci for the world inventory. The natural steady

* See references quoted by Jacobs[3], p. 14.

state level appears to be somewhat higher than this, ~6.9 x 10^7 Ci and corresponds to a production rate of about 0.5 triton/cm^2-sec.[18,3,1]

The world inventory of tritium at the present time is an order of magnitude greater due to the residues from the testing of thermo-nuclear weapons. Assuming no further contribution from this source, the data shown by Petersen, et al.[18] indicate that it will require about 40 years for the decay ($t_{\frac{1}{2}}$ = 12.3 years) to bring this level down to the "natural" level. However, by 1985-1990 the rising yields from thermal power reactors will have brought the tritium to this level. Thus, it appears that the world tritium inventory will never drop below about ten times that resulting from natural sources, and may be 100 to 1000 times as great depending on the types and numbers of nuclear energy sources employed.

Ray[19] has summarized the reactions occurring in a thermal power reactor which lead to tritium production. Chief among these is ternary fission[3] of U or Pu. In the case of U-235 the T yield is 0.87 x 10^{-4} per fission. Other significant sources are: n,T reactions with core construction materials, the $^6Li(n,\alpha)T$ reaction on trace lithium impurities, the n,T reaction with deuterium in the coolant and the production from burnable poisons such as boron. The contribution from photo-nuclear reactions in power reactors is small, about 0.01% of that produced by fission.[19]

Thus, there exists considerable variability in tritium production in power reactors. For example, the tritium yield from Pu-239 is about twice that from U-235[3]. The production from the normal deuterium content (0.015% of the hydrogen atoms) of water is less than 0.1% of the fission yield. However, for

heavy water moderated reactors the yield would be several times that from fission.

In the pressurized water reactor (PWR) a very significant source is the boron used as a "chemical shim", i.e., a chemical added to the coolant to level out the reactivity as a function of time. The rate of tritium production varies with the length of time the fuel has been in service and the coolant turnover rate. An average value would place the contribution from this source about equal to that from fission.[19] This tritium becomes a part of the primary coolant. Boron used in control rods produces significant quantities, but the tritium will be largely fixed within the rods.

It is difficult to estimate the effect of controlled thermonuclear reactor (CTR) development on tritium production. As it is a fuel as well as a product, containment rather than disposal becomes the major problem. The overall tritium hazard does become magnified, however, due to the large quantities involved. On an energy basis it has been estimated that the production rate may be 10^5 times greater than from fission[3], and a single 3000 M watt (th) reactor could burn nearly 10^7 Ci/day, or a fair fraction of the present world inventory.

Table IV presents rough approximations of tritium yields associated with different nuclear reactors.

Prediction of the total environmental tritium level is thus subject to considerable uncertainty. Jacobs[3] lists annual production rates of 2×10^6 Ci in 1980, 6×10^6 in 1990 and 15×10^6 in the year 2000 leading to accumulated values of 6×10^6, 32×10^6 and 96×10^6 Ci, respectively. These data are apparently Cowser's estimates.[20] Petersen's review includes

TABLE IV

TRITIUM YIELDS - 3000 MW (TH) REACTOR

		Curies per day
Thermal fission, U-235		50
Reactivity control (chemical shims),	PWR	10-60
	BWR	2-15
1 ppm Li impurity in primary system		25
Deuterium in light water[(a)]		0.03
Heavy water moderated		80-150
Fast breeder		50-100
Thermal fusion reactor (CTR)		10^6-10^7

(a) assumes doubling of natural D content by n reactions with light water.

contributions from all the sources discussed above and leads to production rates about a factor of 3 greater. It would seem that Petersen's estimates of 2×10^7 Ci in 1980, 10^8 in 1990 and 3×10^8 in the year 2000 might be within a factor of two of the real values assuming (1) power reactors as the major source, and (2) no further H-weapon testing.

There are several aspects that must be considered in assessing the impact to the tritium production: the total production and world inventory, the concentration levels reached in process liquids, e.g., the primary coolant in a thermal reactor, the amounts actually released to the environment and the localization with respect to the environment. With thermal reactors which are the immediate sources of the increased tritium, most of the fission tritium will remain in the fuel until the chemical reprocessing step. With Zircaloy-clad fuels probably only 0.1

escapes from the fuel elements.[19,21] Diffusion through the cladding or effusion through pinholes appear to be the primary mechanisms. The losses are higher by a factor of 10 if stainless cladding is used.[21]

In any case, the reprocessing plant will be handling most of the tritium, probably 50-90%, associated with both thermal reactors and fast breeder reactors. If direct dissolution of fuel is used then the bulk of the tritium equilibrates with water and process chemicals, e.g., nitric acid and organic solvents. Thus, prudent tritium control in reprocessing dictates removal before the dissolution step. Otherwise, the disposal of waste H_2O could become a serious problem.

II. TRITIUM RECOVERY

A. Processes for Deuterium Recovery

Deuterium, the stable isotope of mass 2, was the first isotope separated. Its presence in natural water to the extent of 0.015% makes it readily accessible and the separation has been studied by almost every conceivable means. The requirement for large quantities of heavy water, D_2O, for reactor moderator resulted in the development of commercial processes for separation and purification. Thus, a large amount of data is available on separation processes for deuterium. Barr and Drews[22] list 100 different processes that have been studied. For discussion these can be classified according to the following list:

1. Chemical exchange
2. Distillation
3. Electrolysis and other water decomposition processes
4. Diffusional processes
5. Freezing and zone melting
6. Adsorption-desorption

7. Solvent extraction

To this list we could add:

8. Centrifugation
9. Chromatography
10. Selective atomic or molecular excitation

An excellent review of general isotopic separations methods is given by London.[23]

In addition to the report of Barr and Drews, other excellent reviews of deuterium and heavy water separation are available. The NNES series[24,25,5] cover the development through 1954. Benedict[25] made a comprehensive survey in 1955. Rae[27,28] re-examined the methods from the point of view of producing large quantities of D_2O. A report on Soviet research and development was prepared by Kammermeyer[29]. A very detailed review was made by Levins[30] which compared the methods in use throughout the free world up to 1970. He, along with Barr and Drews, and Rae, considered the potential of several competitive processes. Their data and conclusions are considered in this write-up. Before discussing these summaries a brief discussion of each method is in order.

1. Chemical Exchange

Considering a general reaction of the type:

$$AB + A^{\mp}C \rightleftharpoons A^{\mp}B + AC$$

where A and $A^{\mp}$ are different isotopes, the equilibrium content K_e is different from unity because of the different quantization of the vibrational energy of the molecule. At high temperatures K_e approaches 1 ($\ln K_e = 0$). At low temperatures the maximum value of $\ln K_e$ is the difference in the zero point

energies of the molecules. These are the limiting values for K_e, the partition-function, Q, ratio,

$$K_e = \frac{Q_{A\,B}^{\mp}\, Q_{AC}}{Q_{AB}\, Q_{A\,C}^{\mp}} .$$

The theory of isotope exchange reactions has been soundly developed over a 25-year period starting with the paper of Bigeleisen in 1947.[31] Libby[8] calculated constants for the hydrogen isotopes. Recent reviews are presented by Monse, Ishia and others in Isotope Effects in Chemical Processes[32].

Several generalizations can be made:

a) High vibration frequencies lead to high separation factors, α.*

b) Large differences in vibration frequencies of the reacting molecules AB and $A^{\mp}C$ lead to high separation factors, and would reach a maximum when one of the reactants is atomic.

c) The heavy isotope tends to concentrate in the compound having the higher vibrational frequenty.

---

* The separation factor, α, is defined as $\frac{(1-y)(x)}{(1-x)(y)}$ or approximately $\frac{x}{y}$ where x is the $A^{\mp}/(A+A^{\mp})$ ratio in one phase or chemical compound and y is the same ratio in the other phase or chemical compound. In this particular case K_e is the same as α. Where different numbers of isotopic atoms are involved in each compound, e.g., the reaction $NH_3 + HD \rightleftharpoons NH_2D + H_2$, a numerical factor separates K_e and α.

Since equilibrium constants normally are within an order of magnitude of unity, many stages must be used to separate isotopes in pure form. If separate phases are involved countercurrent flow can provide multiple stages. As an example, consider the equilibrium between hydrogen gas and water. Deuterium favors the water phase. Suppose that the hydrogen is exchanged with water having a normal HDO content in a countercurrent tower. If a portion of the product water, now enriched in HDO, is decomposed to hydrogen gas to flow back into the towers, a continuous enrichment will occur and a small amount of water enriched in HDO may be removed from the tower.

A second approach is simply to use the fact that the equilibria are temperature dependent. Re-equilibration at a different temperature will return part of the enriched product to the other chemical form which can then be recycled. This "dual temperature" approach is often an economical method for isotopic enrichment.

Table V lists some exchange reactions that have been extensively studied.

The H_2O-H_2S exchange is the main reaction employed for heavy water separation and has been demonstrated for large scale production. Commonly called the GS process, G for Girdler, the engineering firm which constructed the plant, and S for sulphide (or perhaps for J. Spevack, who did the early development work on the process at the SAM Labs during World War II).

The process uses a pair of countercurrent gas-liquid contacting towers, one operated at 30°C and one at 130°, where the equilibrium constants are respectively 2.22 and 1.76 for the reaction:

TABLE V

CHEMICAL EXCHANGE REACTIONS FOR DEUTERIUM SEPARATION

Reaction	Separation Factor	Temperature, °C	Comments
1) H_2O-H_2S	1.8 to 2.2	130 to 30	Safety, corrosion problems.
2) H_2O-H_2	2 to 4.5	200 to 5	Catalyst required at lower temperatures.
3) NH_3-H_2	2.8 to 8	70 to -65	Catalyst required.
4) H_2O-PH_3	1.9 to 2.3	130 to 30	Catalyst required.
5) H_2O-HI	2.8 to 3.4	80 to 30	Corrosion severe, azeotrope problems.
6) $N_2H_4(H_2O)$ -H_2	2 to 4	(140-30)	Hydrazine acts as catalyst for H_2-H_2O exchange.

TABLE VI

OTHER PROPOSED EXCHANGE REACTIONS FOR DEUTERIUM ENRICHMENT

7) B_2H_6-H_2	Separation factor not known, requires refrigeration.
8) Hydrocarbon-H_2	Reaction rates low.
9) Mercaptan-H_2O	May be interesting, data limited.
10) Glycol-H_2O	Low separation factor.
11) Aromatics-NH_3	Separation factor probably low.
12) Acetone-H_2	Probably good separation, kinetics poor.
13) Metal-hydride-H_2	Most have low exchange rates, e.g., Th, K, Na, Cs, Pb. Uranium hydride apparently exchange rapidly. Vanadium hydride reported to show unique behavior in that heavy isotope concentrated in the hydride. Separation factors probably low for Gd,

TABLE VI (CONT'D)

	Ce, Li hydrides. Ti hydride reported to have good separation factor.
14) Benzene-HCl	Poor separation factor and rate.
15) HCl-H_2	Poor separation factor.
16) Alizarin-H_2	Separation similar to NH_3-H_2 system.
O-Anisidine-H_2	Reagents costly.
O-Toluidine-H_2	
17) H_2S-MeOH	Similar to H_2S-H_2O process.
18) EtoS-H_2O	" " " "

$$H_2O_{(\ell)} + HDS_{(g)} \underset{\text{hot}}{\overset{\text{cold}}{\rightleftharpoons}} HDO_{(\ell)} + H_2S_{(g)}$$

Water enriched in deuterium is withdrawn at the bottom of the cold tower and moved to a higher stage for further enrichment. The H_2S circulates within the system. Details of the process are discussed in many papers. Barr and Drews use it as their reference process. Bebbington[33] has described the Savannah River and Dana plants. Benedict[26] made comparisons with other large scale processes. Levins[30] has reviewed all the GS plants in operation.

Although quite successful in operation the H_2S-H_2O system has some bad features: H_2S is very toxic*, the system is corrosive, the effective separation factor† is only about 1.26 for a practical dual temperature plant, thus limiting the deuterium

* An inventory of several hundred tons of H_2S is required for a large scale plant.

† The effective separation factor is usually defined as the ratio of the high and low temperature separation factors.

recovery. It is felt that no further significant improvements will be made in the process.

The reaction $H_2O + HD \rightleftharpoons HDO + H_2$ is attractive because of the much higher separation factors and greater temperature coefficient. $\alpha = 3.87$ at 25°, 2.47 at 125°. The disadvantage is that the exchange proceeds too slowly at the lower temperatures without a catalyst.

The plant built at Trail, B. C., used Pt-charcoal and Ni-Cr_2O_3 catalysts at 65°. Hydrogen was produced by electrolysis and the depleted H_2 was used for ammonia synthesis. After several years of operation the plant was closed in 1956. Operating costs were high. Cheaper sources of hydrogen could not be used because of catalyst poisoning. For such a plant a secondary use of high purity by-product hydrogen must help support the operation. Benedict[26] has examined the economics of the process. A detailed description of the Trail Plant is given by Murphy.[25]

Because of inherent advantages mentioned above, consideration of the H_2-H_2O reaction in dual temperature processes has received much attention. Other solid catalysts, high pressure operation, and the use of homogeneous catalysts have been proposed. These are discussed by Levins[30]. A pilot plant was operated in Germany for a short time[34] using towers at 30° and 200° with heterogeneous catalysis. It does not appear that the possibility of finding a suitable homogeneous catalyst has been completedly eliminated. Thus dual temperature operation of a plant based on the H_2-H_2O exchange is still an attractive possibility (a homogeneous catalyst is preferred for kinetic reasons). The catalyst should be cheap, easily recovered from solution, non-corrosive and stable.

In many respects the NH_3-H_2 exchange is even more attractive. For the reaction:

$$NH_{3(\ell)} + HD_{(g)} \rightarrow NH_2D_{(\ell)} + H_{2(g)}$$

the separation factor at 0° is 4.56 and at 100°, 2.73, or about the same as for H_2-H_2O. However, if the process could be operated at -40° and 70°C an overall separation factor of about 2.0 would be obtained. Tests in the German pilot plant indicated more economical production by this route than with the H_2-H_2O process.[35] According to Levins[30], the exchange mechanisms are not completely understood. The metal amides of group I elements are effective catalysts but even with these the reaction rates are low.

Present disadvantages would include: low reaction rates at the low temperatures where separations are high, costs of catalysts, possible need for mechanical agitation. For monothermal operation the cost of ammonia cracking must be included. The monothermal method is attractive because of the high separation factor, 5.8, but requires a large ammonia plant. Levins[30] estimates that a 400 ton/year heavy water plant would require a 6000 ton/day ammonia plant.

A French plant[36] is in commercial production using KNH_2 catalyst and thermal cracking of NH_3 to produce H_2 for recycling. The design capacity is 25 tonnes/year.

The phosphine-water process has separation factors similar to the GS process, but since PH_3 has 50% more hydrogen per mole the contracting tower can be reduced in size. Although many catalysts exist (both acids and bases catalyze the exchange), an ideal one has not been reported. A probable disadvantage is the nature of phosphine gas; toxic, spontaneously flammable and

costly to produce.

Exchange of water with the halogen acids has been considered in some detail. As with the phosphine process, Barr and Drews used it in their comparative study, in this case the HI-H_2O reaction. Vaisberg[37] examined the HCl-H_2O system. The separation factors are greater than for the GS system, the exchange rates are rapid and chemical costs are reasonably low. Major problems do exist. Corrosion is severe, the high solubility of HX in the cold tower and the high vapor pressure of H_2O in the hot tower decrease tower efficiency. (Already HX is carrying only half as much hydrogen as H_2S). The acids also form azeotropes with water. However, the high separation factors at the lower temperature continue to interest workers. It has been proposed that the solid hydrates might be employed[30].

The last reaction in Table V can be thought of as a H_2-H_2O exchange using hydrazine as a catalyst. A new problem is introduced, the necessity of separating hydrazine from water but, on the assumption that this can be solved, Barr and Drews made comparisons with the H_2S-H_2O and the other processes listed in Table V. Their conclusion was that an exploratory investigation of the reaction was needed.

The processes listed in Table VI while interesting from a fundamental viewpoint do not at present appear attractive for large scale use. Several are worthy of further study for specific applications. Also, it must be noted that many interesting reactions have yet to be uncovered and there is lack of understanding of the mechanisms of those listed; for example, the metal hydride-hydrogen exchange reactions. They vary greatly in rate. Also, while normally the light isotope concentrates in the hydride, recent data indicate that with vanadium the heavy isotope is

concentrated.[38]

2. Distillation

The separation factors for distillation can be taken approximately as the ratio of the vapor pressures. Boiling point data from Tables I and II suggest that reasonable separations could be obtained. Other compounds that have been proposed are ammonia and methane. Table VII lists data from Benedict[26] for the four compounds considered.

TABLE VII

DEUTERIUM SEPARATION FACTORS - DISTILLATION

Compound	Vapor Press Ratio* Triple Point	b.p.	Boiling Point °C	Triple Point
H_2/HD	3.61	1.81	-252.9	-259.4
$(NH_3/ND_3)^{1/3}$	1.080	1.036	- 33.6	- 77.7
$(H_2O/D_2O)^{1/2}$	1.120	1.026	100.0	0.0
CH_4/CH_3D	1.0016	.9965	-161.9	-182.5

* Assumption is that, $P_{H_2O}/P_{HDO} = P_{HDO}/P_{D_2O} = \left(P_{H_2O}/P_{D_2O}\right)^{1/2}$, etc. and that isotopes are randomly distributed in ideal solution.

The distillation of liquid hydrogen is attractive because of the high separation factor, 1.8, and relatively low power consumption. It was used by Urey[39] for the original concentration of deuterium and a flowsheet was later developed by Clusius[40]. A plant was considered by the USAEC but apparently abandoned due to lack of industrial experience at very low temperatures. Several small plants are in existence throughout the world, the largest apparently in India with a capacity of about 14 ton/year[41].

It is not economical to produce H_2 solely for the purpose of separating D_2. Thus such an isotope plant must be an adjunct to another plant utilizing large amounts of H_2 such as an ammonia plant.

Water distillation, while not as attractive fundamentally, has been proposed for practical reasons. The temperatures are convenient, permitting low grade heat, no chemical processing is involved and the technology is straightforward. The principal application has been for upgrading partially enriched D_2O. At the Savannah River plant water distillation is used to enrich D_2O from about 15% to 90%. The distillation is carried out at 100-torr pressure and operates with a separation factor of 1.05.[42] A basic problem is that at temperatures low enough to give good separation factors, the capacity of the distillation equipment is low.

Ammonia distillation has several advantages over water distillation: greater separation factor, higher hydrogen content per mole and lower heat of vaporization. Disadvantages include the necessity of higher pressure operation and/or use of refrigeration equipment and corrosion problems. Barr and Drews conclude that it is not competitive. On the other hand, it would probably be very useful for upgrading NH_3 which was partially enriched by a successful NH_3-H_2 exchange plant.

Methane distillation suffers from low separation factors although some evidence exists that these are improved at high pressures. The interest is largely that methane is potentially an excellent, concentrated source of deuterium.

E. Electrolysis

Until 1943 all commercial heavy water was produced by electrolysis. The electrolytic hydrogen plant at Rjuhan, Norway,

produced about 1.7 tons per year using a cascade arrangement. The plant at Trail, B. C., used electrolysis to refine the product from the H_2O-H_2 exchange reaction. Separation factors as high as 8 have been found. Thus, for the refinement of highly enriched water the power costs can be tolerated. Benedict[26] has considered the economics of several plants using electrolysis as part of their overall process. As noted before, a market for electrolytic hydrogen is a necessity to make the process competitive.

In the process the heavy isotope is concentrated in the cell while the H_2 is depleted. This is consistent with the equilibria $HD + H_2O \rightleftharpoons HDO + H_2$, $K > 1$. However, the separation factor found is much higher, $\alpha \sim 8$, than given by the exchange reaction. Thus other processes, probably involving diffusion and electrode phenomena, are important. Although there has been considerable research on the effects of electrode material, electrolyte composition, temperature, current density, etc., the process is still not completely understood. Levins[30] has summarized much of this work.

Some novel approaches have been suggested: reversible electrolysis[22], and energy recovery with fuel cells.[43] The possibility of finding a resonant phenomena at the electrode such that D_2 could be preferentially discharged has been envisioned by many workers. Although this may exist--in principle--the resonant frequency may be outside any usable range.

Electrolysis of other compounds is also a possibility although apparently ammonia is the only one seriously considered.[44]

Other decomposition reactions of water such as the reaction with active metals may show separations governed by the principles

which determine exchange reaction equilibria. A unique case involves radiolytic decomposition since highly reactive species, some of which are monatomic, are produced. Large separation factors are expected for some processes. While the reactions are of theoretical interest they are normally non-specific and inefficient. Some further observations are made in section IV B.

4. Diffusional Processes

Several processes can be described under this heading. The simplest is effusion or the movement of gaseous molecules through small holes under the condition where flow is governed solely by molecular velocity. "Barrier diffusion" is the practical development. Separation factors are given by the square roots of the molecular weights.

Thermal diffusion depends on the transport of momentum in collisions. The thermal diffusion separation factor is given by $(m_2-m_1)/(m_2+m_1)$. Though the theory is incomplete, the long usage and success of the hot wire column developed by Clusius and Dickel[45] has built up a backlog of knowledge that applications of the method are routine.

Both processes would work with either H_2 or H_2O; however, there is little incentive to use them because although the separation factors are high compared to those for other isotopes for which the methods have been very successful, in the case of hydrogen isotopes other superior methods are available.

5. Centrifugation

Although not related to diffusion, the separation by centrifugation is purely physical and the separation factor depends on

mass difference.* There is little to be gained over other methods for very light atoms and, in fact, only becomes competitive for higher mass isotopes.

6. Freezing Phenomena

When water freezes, the heavy isotope concentrates in the ice. As with distillation, the separation factors can be predicted from the ratios of the vapor pressures. These turn out to be small, about 1.02 for H_2O-D_2O separation. Another problem is that it appears necessary to carry out the freezing step very slowly.

Zone melting can be thought of as a continuous multistage freezing-melting process. It appears quite useful for purification of small quantities of solid compounds but further discussion here is not pertinent.

7. Adsorption Phenomena

Vapor pressure differences can be realized and sometimes magnified by adsorption of molecules on an active solid surface. Typical adsorbents are charcoal, alumina, silica and molecular sieves. Each has some potential for use with H_2 at low temperatures or with water at ordinary temperatures. In general the higher isotope has a greater heat of adsorption and this can utilize less active sites. This should lead to an enhancement of separation factors. This is confirmed by data for H_2O-HDO on charcoal as quoted by Barr and Drews[22].

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* Actually α is given by the exponential, $e^{(m_2-m_1)V^2/RT}$, where V is the linear centrifugal velocity.

TABLE VIII

α-H_2O/HDO FOR CHARCOAL ADSORPTION

Temp°C	Charcoal Adsorption	Distillation
30	2.8	1.07
100	1.214	1.025

Although the method is simple there are many difficulties in designing a large plant. The amount of water adsorbed per pound of charcoal is small. Adsorption is basically a batch process and it is very difficult to construct a multistage plant. There does seem to be some potential for using adsorption as a single stage plant to feed another type separation plant[22].

Adsorption is conveniently studied by gas chromatographic (G-C) methods[23]. One of the first studies used palladium black[46]. Other packing materials used are activated alumina, silica and molecular sieves[47]. Excellent separations can be achieved because of the reasonably high α value and the very large number of theoretical plates. At low temperatures ortho and para forms of H_2 and D_2 are separated.[48,47] Although excellent for analytical use and theoretical study, GC methods have only recently been considered for larger scale operation. Timmins and Ryan[49], Clayer[50] and others have projected the method to commercial processes. Levins[30] concludes that further examination of this method is worthwhile.

8. Solvent Extraction

Solvent extraction is similar to distillation in that the process involves partition of species of different vapor pressures, or more precisely of different thermodynamic activity,

between two phases. The process is different in that in distillation the separation is determined by the aqueous phase, the other phase, vapor, being approximately a perfect gas. In extraction the activities of the species in the organic phase may also differ, thus enhancing or decreasing the separation factor. Augood[51] considered the possibility of separating H_2 and D_2 using solvents such as H_2O, CH_4, H_2S, Ne, N_2, etc.

Kirschenbaum[5] lists measured solubilities of H_2O and D_2O in various organic solvents. The solubility ratio H_2O/D_2O at 25°C varied from 1.43 for triethylamine to 1.03 for quinoline. Since the vapor pressure ratio at 25° is about 1.14, this implies preferential extraction of H_2O by Et_3N and of D_2O by quinoline.

Possibly with data such as these in mind Skripov[52] tried extractions with triethylamine. His results were not promising. However, a Japanese patent[53] describes experiments with higher amines that show separation factors of 1.4 or greater.

There appears to have been no attempt to utilize the tremendous store of solvent extraction information that has been developed over the past 20 years to design simple scouting experiments. Potential problems would include solvent inventory and solvent losses. However, it is simple and easily adapted to engineering practice. Power costs should be modest. Some further study seems warranted.

Ion exchange can usually be considered similar to solvent extraction. In the case of water pickup by the resin, this is surely the case. Thus the observation that Kakihana's data suggest water adsorption rather than exchange[30] it not surprising

for in all these processes it is hydrogen bonds that are broken and reformed. In this sense adsorption phenomena on solids are similar.

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The various surveys for heavy water production suggest that the present competitive processes will not drastically reduce the cost of heavy water. On the other hand, there is general agreement that the GS process has about reached its ultimate development. Several factors should be kept in mind in evaluating these processes: 1) Some processes, like the H_2-H_2O exchange, await a particular scientific development--in this case a homogeneous catalyst. 2) An ideal process for concentrating 15% D_2O may not be economical for water that is 0.015% D_2O, etc. 3) The goals of the process, e.g., high recovery of a specific isotope, high enrichment of another, high decontamination of a large volume from another isotope, etc., may each place different restrictions on the choice. 4) Other processes such as chromatography or solvent extraction have not been fully investigated. Finally, there is always the possibility of a new concept. Molecular excitation which is discussed in the next section falls in this category.

B. T_2 and T_2O Separations Methods

The principles and derived separations methods discussed for deuterium apply to tritium. The mass is higher, the zero point energies are lower, leading to greater separation factors. An additional factor is the radiation energy associated with the decay. As was noted earlier, this tends to promote chemical reactions.

The discussion in this section will follow basically the same outline as for deuterium.

1. Chemical Exchange

Table IX shows typical differences in equilibrium constants between deuterium and tritium. In this case the exchange is between water and HD or HT. Experimental data agree well with theory.[8,54] Thus, those methods which were shown to be best for deuterium will be excellent for tritium. At this point, however, we will modify the criteria and make the assumptions that we are dealing with large volumes of water containing a very low concentration of tritium, and that we are interested primarily in decontaminating the water. A secondary goal will be to concentrate the tritium removed. In the deuterium problem, removal of all the deuterium was never an issue.

Because of the large volumes of water to be treated and the low concentration of tritium (An order of magnitude number of 1 μgm/ℓ or 10 μCi/ml will be assumed for reactor coolant. This level is about 3000 times the MPC for water.), a high separation factor is desirable. Chemical exchange is thus a good candidate. Further, a process involving water as a reactant is almost mandatory. Referring to the discussion of the last section and Table IX, it is seen that H_2-H_2O exchange operating on a dual temperature basis between 100°C and 400°C would give an overall separation factor of about 2.0. A homogeneous catalyst, permitting a liquid water phase, and lower temperatures, for the cool part of the cycle would permit an overall separation factor of greater than 3.

The other exchange reaction discussed in Section IV.A could be used. Jackson[55] has computed the equilibrium constants for

TABLE IX

EQUILIBRIUM CONSTANTS FOR THE HYDROGEN-WATER EXCHANGE REACTION (THEORETICAL)[8]

Temperature	HD + H_2O	HT + H_2O
20	3.78	6.24
100	2.65	3.83
200	2.09	2.65
300	1.75	2.09
400	1.54	1.77
500	1.37	1.52

the H_2S exchange reactions involving tritium for the reaction:

$$HTS + H_2O \rightleftharpoons HTO + H_2S$$

and found K = 2.86 at 30°C and 2.15 at 130°C. Corresponding values for the HDS + H_2O reaction are 2.22 and 1.76, respectively. The NH_3-H_2 cycle would give higher separation factors but the reaction is not as easily applicable to the water problem.

2. Distillation

From Table I it is seen that the boiling point of T_2 is 25.0°K and of HT is 22.9°K compared to 20.4°K for H_2. Thus, as with deuterium, distillation of the elemental form is a practical scheme. The scheme that probably is most attractive economically is to combine distillation with another separation process that requires hydrogen such as chemical exchange or adsorption. One of the reasons that hydrogen distillation has not been the large scale source of deuterium is that it is not economical to produce hydrogen for the sole purpose of separating deuterium. Rather, the isotope plant must be an adjunct to another plant which uses

hydrogen. The ground rules for tritium removal from water may not include this limitation.

If adequate separations could be achieved, the distillation of water would be the simplest and most straightforward approach. Heavy water separation by this method was discussed earlier. Vapor pressures of all the isotopic species of water are known. Van Hook[56] has calculated parameters for the equation

$$\ln \frac{P_{H_2O}}{P_x} = \frac{A}{T^2} + \frac{B}{T} + C$$

for 18 different isotopic water species over the temperature range 0-130°C. Jones[7] measured the vapor pressures for the pure liquids D_2O and T_2O compared to H_2O.

Other data on T_2O were obtained by Popov and Tazetdinov[57] and on HTO by Merlivat[58]. Jackson[55] recalculated the ratios. His results agree quite well with Van Hook's. Using Van Hook's equation and data, the values in Table X were calculated.

The measured liquid/vapor T ratios of Sepall and Mason[59] gave 1.1 at 25°, 1.06 at 50° and 1.03 at 90°.

The power consumption for distillation of water would be rather large because of the number of stages required. If the distillation were carried out at about 60°, $\alpha = 1.05$, about 400 stages would be required to reduce the tritium content from 10 μCi/ml to 3×10^{-3} μCi/ml. If α for the process were 1.5 only 50 stages would be necessary.

This constitutes the stripping, or decontamination section of the plant. The concentrated tritium would then pass into the enrichment section. This section rapidly becomes smaller in size

TABLE X

VAPOR PRESSURE RATIOS FOR ISOTOPIC WATER SPECIES P_{H_2O}/P_x

Temperature °C	T_2O	DTO	D_2O	HTO	HDO
25	1.193	1.175	1.154	1.095	1.075
50	1.134	1.123	1.110	1.065	1.053
100	1.064	1.060	1.052	1.030	1.026

and it is here that alternate methods might be utilized.

In spite of the large heat requirements for stripping by distillation, it should be noted that only low grade energy is required and the process could perhaps utilize waste heat from a reactor.

3. Electrolysis

Electrolysis has long been used to concentrate small quantities of tritium for analyses.[60,61] Foster and co-workers[62] performed experiments at higher tritium concentrations, 20-30%, and determined that radiolysis from the tritium did not affect the separation. Their values for α were 5.6 for H-D, 1.9 for D-T and 10.4 for H-T. Johnson, et al.[63] described a multiple stage process to produce high purity tritium. Catalyst recombiners produced water for the next lower stage.

The technology is well developed, the process is probably the simplest of all, the separation factor is the highest, the capital costs would be small and there is no doubt that an electrolytic separations plant would do the job. The big factor, of course, is electric power. About 25 kW-hr are required to

electrolyze a gallon of water. Thus to decontaminate a gallon of water 5 stages and enrich the recovered tritium might require 100-200 kW-hr. To process the 10^5 gal inventory in 40 days would require an average power of 10^4 kW. Ray[64] and others have proposed recovering part of the power through the use of H_2-O_2 fuel cells in place of catalytic recombiners.

The fact that the separation factors are much greater than simple H_2O-H_2 exchange indicates, is intriguing, and some thought has been given to possibly increasing this further, or perhaps utilizing the high separation without separate gas recombiners. The latter idea, "reversible electrolysis," was proposed by Barr and Drews[22]. Other workers have proposed finding a resonant process which would reverse the separation and produce gas enriched in tritium. Further investigation of isotope separation at electrodes is needed. It should be noted in passing that attempts to produce more efficient electrolysis per se, i.e., by lowering the overvoltage may be self defeating for the high separation factors observed may result from the same factors which lower the electrode efficiency.

4. Diffusion, Centrifugation, Etc.

These methods, based on mass effects, were discussed in Section IV-A. Applying each to the tritium problem introduces no new factors. Thermal diffusion is a simple, easily controlled process and might have application in the enrichment end of a tritium separation plant. Verhagen and Sellschop[65] described a two-stage laboratory scale column with which they obtained enrichments of up to 800. Almquist[66] used a 3.5 m column and obtained equilibrium enrichments of 680.

5. Radiolysis

Isotopic effects are expected in radiolytic decomposition and it is natural to question the phenomena in the case of tritium. Because of the complex nature of radiolytic reactions, especially in aqueous solution, such studies would have theoretical interest. Matheson and Dorfman[67] have compared rate constants observed by several workers for free radical and solvated electron reactions. The rates are generally higher with H_2O, ranging from a difference of a few percent to a factor of 10. No references have been found to experimental work showing molecular yields for different isotopic species from radiolytic reactions.

6. Adsorption and Chromatography

As was noted in Section II A, the separation factors found on adsorption-desorption are significantly greater than that given by vapor pressure ratios, thus implying an adsorption site selectivity. Although one might expect greater separation differences where the differences in energies between the vapor and adsorbed states were greater, the α values shown in Table VIII for charcoal adsorption of water indicate that weak intermolecular forces can be very significant.

Considerable information on separation of isotopes in the elemental form is available from gas chromatographic studies. Glueckauf and Kitt's[46] experiments with palladium black showed that complete separation of D_2 could be achieved by displacement chromatography with a column 44 cm in length, and projected their experiments to the concentration of small quantities of tritium. It is interesting to note that palladium catalyzes the exchange reactions so that only the pure isotopic species

are obtained, i.e., D_2 and T_2.

Several successful experiments using elution chromatography were carried out during this period. Smith and Hunt[68], using a chromia-alumina packing at 77°K, obtained isolated peaks for H_2, HD, and D_2 on an analytical scale. Smith and Carter[69] extended the studies to tritium using packings of palladium coated silica, silica, alumina, alumina-chromia and alumina-ferric oxide. No separation was obtained with Pd-silica. The best separation was obtained with activated alumina. The column was operated at 77°K, using He carrier. Gant and Yang[70] had previously shown a similar separation on a molecular sieve column obtaining H_2, HT, and T_2 from a feed containing 1 atom % T. No attempts were made to determine separation factors for these systems. Some work has been reported on gas chromatographic separation of isotopically substituted organic molecules.[71,72]

Although adsorption-desorption processes have been shown successful, the only extensive data appear to be on the systems H_2-palladium and water-charcoal. The latter process would seem worthy of consideration for the tritium separation problem. A vapor pressure ratio P_{H_2O}/P_{HTO} of about 2 might be expected at 30°C. It may turn out, however, that the charcoal bed volume would be prohibitively large. Barr and Drews[22] in their evaluation for a heavy water plant use an adsorption capacity of 1 kg water per 1000 kg charcoal and a cycle time of two hours. At $0.75 per kg for charcoal and tankage costs, the costs and plant size become large.

Gas chromatography is usually considered an analytical type operation and is essentially a batch process. However, it can be made semi-continuous by cyclic operation or by a moving bed

process. Columns up to 4 ft in diameter have been reported[73] so the device has definitely moved out of the laboratory. Applied to hydrogen gas, if one assumes a separation factor of 1.5 and a stage height of 5 cm, impressive separations can be achieved. However, flow rates are small and costs of refrigeration are high.

7. Solvent Extraction

There are numerous concepts for separations based on different thermodynamic water activities. Distillation, adsorption, and freezing have been discussed. Other methods would include separation of salt hydrates from solution and solvent extraction. The latter technique is easily adapted to large side operation and merits further consideration here. The basic concept as indicated in Section IV A is hydrogen bonding to molecules of the solvent. Since the escaping tendency of H_2O from an aqueous phase is greater than for HTO a solvent which forms stronger bonds with H_2O than with HTO would be expected to show greater separation factors than for simple distillation at the same temperature. Alternatively one could override the vapor pressure effect and selectively extract HTO.

For most systems the substitution of T for H results in a lower bond energy and an expanded structure. This is the result of many factors: the lower zero point energy, the strong anharmonicity (greater in the case of the T-O bond) and the resulting effect on intermolecular forces. Although the hydrogen bond strength in liquid water is probably greater with HTO (or T_2O) than with H_2O, it is generally considered that H-bonds in complex molecules are weaker when a heavy isotope is substituted. Structural (geometric) factors become important and at

present it is not possible to predict the magnitude of the isotopic effect in extraction.

However, we know a great deal about the thermodynamics and mechanisms of solvent extraction including the number of water molecules per molecule of solvent of many organic-aqueous systems. In addition, we have other fundamental data to rely upon including solubility measurements in D_2O and H_2O[74], dissociation phenomena in isotopic waters[75] and optical absorption data. With respect to the latter, Shatenshtein[76] has for example measured the infra-red O-D bond shifts for H_2O and CH_3OH in a variety of organic solvents. Comparable data for O-H bonds which should be available would permit predictions of solvent extraction separations. Rabinovich[77] has tabulated data on solubilities, heats of solutions, vapor pressures and other pertinent thermodynamic data showing the isotopic effect in water-organic systems. We are thus in a position to make a systematic survey of different classes of solvents. It seems reasonable to expect that some may provide separation factors much greater than found in simple distillation. Table XI lists some solvents that are chemically different and which often form different types of complexes. Within each class there is a wide choice of organic compounds such that one may adjust the polarity, vapor pressure, water solubility and other physical properties.

Some of the potential advantages include: 1) either vapor-liquid or liquid-liquid extraction can be used, 2) operation at low temperatures where the isotope effects are a maximum is possible, 3) countercurrent operation, giving a large number of stages per extraction unit , is easily accomplished, 4) the technology is well known and has been demonstrated on a large

TABLE XI

CLASSES OF ORGANIC SOLVENTS

Neutral organosphosphorus compounds
Ethers and ketones
Acid organophosphorus compounds
Alkyl or aryl amines
Amine salts
Alcohols
Halogenated compounds

scale. The simplest concept for application of either liquid-liquid or liquid-vapor would be a dual temperature process for extraction and stripping.

Several problems appear: 1) the very low concentration of HTO in the feed water and the large number of stages required implies a large plant with attendant inventory costs for solvent: 2) the solubility of the solvent in water may be a problem. Using high molecular weight solvents to keep the solubility low means lowering the water carrying capacity of the solvent, 3) tritium exchange with hydrogen atoms of the solvent molecule will occur to some extent. If the exchange rates are low this should not be a serious problem.

Modifications of the water extraction procedure would include modifying the water activity in either or both phases by adding a third component, or alternatively one might take advantage of the isotopic shifts in ionization equilibria such as

$$H_3O^+ + HTO \rightleftharpoons H_2TO^+ + H_2O$$

by extracting an acid instead of water. Salomon[78] has computed a number of equilibrium constants for tritium ionic species in water. Measurements of pK values of various weak acids in H_2O and D_2O by McDougall and Long[79] are illustrative of ionization effects in solution.

In spite of the possible limitations of the solvent extraction method there are so many possibilities and the laboratory investigations are so simple that it would seem wise to obtain sufficient data to permit an estimation of process costs.

8. Molecular Excitation

The concept of isotopic separation by spectroscopic excitation is an old one and was examined in detail for uranium separation. Later, comprehensive experiments and evaluations were made by Gunning[80] using mercury isotopes, London[23] and Smith[81] have reviewed the principles and possible applications. These studies involved electronic excitation for which the absorption lines are very narrow and extremely closely spaced. The approach suggested here is different and involves direct vibrational excitation of the bond involving the isotope, e.g., the O-T bond in water and subsequent reaction with another species X to form TX which is then isolated. The key to the process is that raising the vibrational level of the bond involving T (or H) above the ground state will permit reaction with a low activation energy and thus increase the reaction rate of that isotope. (The reactant X will be chosen such that the normal reaction with OH or OT bonds has an appreciable activation energy, i.e., the rate is very small until the bond is excited.)

Two or more laser beams can be employed to pump the vibrational band to higher vibrational levels if necessary. The most

difficult part of the process may be in the choice of the reagent, which must react with the activated bond before the excitation energy flows into other bonds.

A modification of the process would be to use the excitation to promote one-half of a dual-temperature chemical exchange cycle. (Theoretically, selective excitation may be considered as raising the temperature of the selected bond--and only that bond--to a very high temperature.) Thus, the exchange reaction $H_2 + HTO \rightleftharpoons HT + H_2O$ which normally has an equilibrium constant, K, < 1.0 could be shifted to give K >> 1.0, or alternately shifted further in the opposite direction, depending on whether the O-T or O-H bond was excited. Another possible equilibrium which might be quite suitable is the water-gas reaction.

$$CO + H_2O \rightleftharpoons H_2 + CO_2$$

Here the equilibrium could be shifted to produce either the light or heavy isotope in the hydrogen gas form. Excitation would be provided by a laser tuned to the frequency of the molecular vibration. The hydrogen isotope system is ideal for application of the technique because the vibrational bands for the isotopic species are widely separated. Fundamental frequencies for the water vapor molecules are listed in Table XII.

J. R. Morrey[82] has made extensive calculations on the activation of chemical reactions by infrared laser beams.

The development of high power lasers of the correct frequency makes this approach entirely feasible. Application to the tritium separation problem is particularly attractive because of the very high separation factors that are possible. Mayer[83] is apparently the first to demonstrate that the

TABLE XII

VIBRATIONAL FREQUENCIES OF WATER VAPOR MOLECULES[a]

	T_2O	DTO	HTO	D_2O	HDO	H_2O
ν_1	2235	2304	2291	2671.46	2726.73	3656.65
ν_2	996	1092	1340	1178.33	1402.20	1594.59
ν_3	2368	2737	3708	2788.05	3707.47	3755.79

(a) Calculated values. Tritium containing molecules from Staats[83]; other data from Benedict[84].

principle of selective excitation of bonds does occur and separated D from H by reaction of methanol with bromine on excitation with an HF laser.

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Rae[27] has classified isotope separation processes into three types: high energy, high volume and low energy-low volume. It has been noted that the principal problem in tritium removal is the large volume and the low concentration of tritium. Thus, most processes become high volume ones and many are high energy. Water distillation could do the job but the size of the plant and power costs are huge. Jansen[86] made preliminary estimates for distillation and concluded that the cost would be prohibitive.

Solvent extraction suffers from the same limitation--the size of the plant. However, here there is a possibility of reduction in size because of greater separation factors. Likewise, adsorption processes have the same problems since the

separation factors for all known systems are small. Chemical exchange using the H_2-H_2O reaction might be a good candidate if a homogeneous catalyst could be found. Obviously the only process that is attractive is one with a very high separation factor--a Maxwell's demon type device which will pluck tritium atoms out of a stream of H_2O. The only one of the eight processes discussed that is selective in this sense is the one involving molecular vibrational excitation.

V. STORAGE OF TRITIUM

The tremendous volumes of water that must be processed at the reactor or reprocessing plant are of major importance in determining the feasibility of a tritium stripping operation. An indication of the very low concentration involved is seen from the calculation that under the worst conditions the tritium in 10^5 gallon of reactor coolant would occupy a volume of only a few ml if extracted as T_2O.

It should be noted that the natural deuterium level in the water places its concentration at 10^4 times that of the tritium. Two facts emerge: 1) tritium will exist as DTO quite early in the enrichment section of the plant, and 2) the plant will concentrate a sizeable quantity of heavy water, perhaps 1,000-2,000 lbs. from the water inventory assumed above.

Even though separation of T from D is more difficult than T from H, the small volumes involved probably mean that the cost of the final concentration of DTO is insignificant. The final question then is concerned with fixing the DTO (or DT, T_2 or T_2O) in a form suitable for permanent storage.

Several alternatives appear with regard to disposal or

storage, 1) snip the DTO concentrate to a heavy water recovery plant for reprocessing, 2) dispose of the product in an ice field or in an ocean location where the half-life gives adequate guarantee against entering the biosphere, 3) employ controlled storage, in sealed containers or a non-labile compound. Ray[19] has discussed the "iceberg" approach in connection with the PM-3A site. A tritium concentration of up to 1.5 μCi/ml can apparently be tolerated in ice without the equilibrium vapor becoming greater than the restricted-area MPC.

Only the controlled storage concept would require significant development work. The main question here is the choice of compound. Its radiation and thermal stability, solubility, or hydrolysis characteristics, and exchange rate with other compounds are important parameters. The hydrates of radiation-stable inorganic compounds are possible candidates. Metal hydrides are perhaps better. Pure water is another possibility. In each case dissociation to the elemental form will need to be investigated. Catalytic recombiners could be considered here. Finally, storage of the elemental gas under pressure with liquid or solid adsorbers present can be considered.

VI. SUMMARY AND RECOMMENDATIONS

The properties of tritium have been briefly reviewed. The potential radiation problem resulting from tritium production in power reactors has been surveyed. It is seen that in about two decades the rate of production and the increasing world inventory may dictate controlled storage of tritiated waters. Public opinion may force it before that time.

Since isotope separation may be the only route to controlled storage, the known methods for deuterium separation (heavy water production) have been surveyed and then considered

for tritium separation. Because of the extremely low concentration of tritium and the large volume of water, the problem is formidable and with present technologies may be prohibitively expensive. A process with a high separation factor is required.

Of those available, electrolysis and recombination would work but the power costs are too great. Chemical exchange using the hydrogen-water reaction fits naturally to the problem and the separation factor is good but to retain an adequate separation factor will require developing a catalyst which will be effective at low temperatures.

Solvent extraction is seen as a possible technique and a few relatively simple experiments would determine its feasibility and also add greatly to our knowledge of isotopic processes.

The most novel approach is selective excitation of molecular vibrations. This populates the higher energy levels of the bond involving the isotopic species in question and allows it to react at a greatly increased rate. With the recent availability of tuned lasers to provide the selective energy input, the concept appears quite feasible.

It is recommended that several tasks be undertaken with the goal of finding a solution to the tritium problem before it becomes acute:

A. Economic evaluations should be made of those isotope separation processes which appear to have the best potential. The problem of decontaminating 10^5 gallons of water containing 1 to 10 μCi/ml to a level of MPC or perhaps 1% of MPC should be considered. Separately the concentration (enrichment) of the separated HTO should be considered.

B. The state-of-the-art of catalysis of the $H_2 + H_2O$ exchange should be studied to determine the possibility of finding a low temperature homogeneous catalyst. This would permit development of a dual temperature process with a moderately good separation factor. Other possible exchange reactions should also be considered.

C. Scouting experiments should be performed to determine the separation factors, using solvent extraction of water. Candidates from different classes of solvents where the mechanisms are known to be different should be investigated and the results correlated with information on hydrogen bonding, etc. If reasonably good separation factors are found (overall α greater than for water distillation), then an economic evaluation should be made.

D. Data on adsorption and absorption by solids should be re-examined and evaluated. The information on charcoal is fairly extensive and could serve as a reference. Other materials that should be considered are the usual adsorbents, mentioned in Section IV A, 7 and IV B, 6 as well as a variety of ion exchange resins that have been developed during the last few years. In principle, these solids have two features that can be very significant in distinguishing between similar molecules; site selectivity caused by surface defects and openings of molecular dimensions. Some experimental work will be required.

E. Experiments to test the concept of selective molecular excitation should be carried out. Battelle-Northwest has examined the theory of this process in considerable detail. The necessary equipment (tuned lasers) is now available. This approach should be seriously considered for it is the only method that can give a very high separation factor.

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